



Design of MoFe/Beta@CeO₂ catalysts with a core–shell structure and their catalytic performances for the selective catalytic reduction of NO with NH₃



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ABSTRACT

MoFe/Beta@CeO₂ core–shell catalyst was designed with nano-size Beta supporting MoFe bimetallic oxides as the core and CeO₂ thin film as the shell. The structure and physico-chemical properties of the coated and uncoated CeO₂ catalysts were characterized by TEM, SEM, XRD, N₂ adsorption-desorption, XPS, XANES, ICP-AES, NH₃-TPD, H₂-TPR and in-situ DRIFTS. The catalytic activity tests for NH₃-SCR of NO indicated that the catalyst coated by CeO₂ shell exhibits a remarkable improvement of deNO_x activity, excellent tolerance to SO₂ and H₂O, as well as high thermal stability. The both chemisorbed oxygen species (O₂[−], O[−]) and specific surface area increased for the catalysts after the coating of CeO₂ shells. CeO₂ shells not only increase the acid amount but also improve its acid strength, which could be beneficial to improving NO oxidation to NO₂ during NH₃-SCR. Furthermore, there is a strong interaction among the iron oxides, molybdenum oxides and CeO₂ shells. CeO₂ shells can serve as an effective barrier to inhibit the active metal oxides nanoparticles from aggregating at high temperature. As a result, the coated catalyst with CeO₂ thin film shows a better thermal stability than the uncoated one. What's more, CeO₂ shells can not only suppress the formation of ammonium nitrate and sulfate species blocking the active iron sites but also restrain the generation of iron sulfate, leading to a higher SO₂ and H₂O-tolerance. The above results demonstrate that the design of a core–shell structure catalyst is favorable for improving the performance of deNO_x catalysts.

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1. Introduction

Nitrogen oxides (NO_x) originating from mobile sources, especially the diesel vehicles, contribute greatly to air pollution [1]. So far, the selective catalytic reduction (SCR) of NO_x with NH₃ is considered as the most promising technology [2]. The typically commercial V₂O₅-WO₃(MoO₃)/TiO₂ catalysts for NH₃-SCR have been widely used for decades [3]. Nevertheless, some inevitable disadvantages still remain, for instance, the toxicity of vanadium species, the poor low-temperature catalytic activity, the low N₂ selectivity and the high activity for oxidation of SO₂ to SO₃. These factors greatly restrict its application for the deNO_x process in industry [4,5]. Therefore, it is necessary to develop V-free

deNO_x catalysts with high catalytic activity, excellent H₂O and SO₂-tolerance, as well as high thermal stability [6,7].

Zeolite-based materials, such as SSZ-13 [8], SAPO-34 [9], ZSM-5 [10], FAU [11], HBEA [12], MOR [13] and USY [14], have attracted much attention due to their good adsorption performance and flexibility in active temperature window. There is a significant interest in developing zeolite-based catalysts for NH₃-SCR. Meanwhile, attracted by their superior SCR performance and N₂ selectivity in a wide operation temperature range, Fe exchanged zeolite have been extensively studied in the NH₃-SCR reaction over the past decades [9,15–17]. However, the low-temperatures catalytic activity of Fe-based catalysts still needs improvement [18,19]. What's more, the high concentration of SO₂ in the diesel vehicle exhaust can lead to the loss of the active Fe oxides species [20]. Consequently, SO₂ poisoning is a great challenge for the preparation of high activity of low-temperature NH₃-SCR catalyst. Molybdenum, which is usually introduced as a promoter for improving catalytic activity and enhancing SO₂ resistance due to its unique redox property, has been

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reported in many fields [21–23]. It is also promising to improve the ability of SO_2 -resistance and stability of FeO_x metal oxide catalysts.

Core–shell catalysts (CSCs), constituted with cores (inner materials) and shells (outer layer materials), have drew enormous attention due to their interesting properties as well as utility in the diverse areas including nano-catalysis, magnetite-supported catalysis, nano-electronics, integrated catalysis, etc [24,25]. In most cases, the CSCs show superior properties than either core or shell material alone. For example, Mitsudome et al. [26] reported AgNPs@CeO_2 CSCs to be employed in the reaction of nitrobenzene reduction, which exhibited better catalytic activity than Ag NPs (nanoparticles) alone due to the fact that the presence of CeO_2 can prevent the migration and agglomeration of Ag NPs. Zhang et al. [27] prepared a *meso*- $\text{TiO}_2\text{@MnCe/CNTs}$ core–shell catalyst to be used in NH_3 -SCR reaction. The results revealed that the *meso*- TiO_2 sheaths greatly improve the SCR activity, SO_2 -tolerance and stability of the coated catalyst compared with the uncoated one. Nevertheless, the hydrothermal stability of this catalyst is so poor that it is easy to be collapsed at the high reaction temperature ($>500^\circ\text{C}$) [28]. What's more, the weak acid of CNTs (carbon nanotubes) is unfavorable for the adsorption and activation of NH_3 . In contrast, Beta zeolite possesses a stronger acidity and better hydrothermal stability. Moreover, compared with the CHA-zeolite catalysts, Beta zeolite possesses a larger pore size, which is not readily blocked by the outer oxide shell. Therefore, it can enhance the access of reactant molecules to the catalytically active center. Of course, as the core materials, the size of Beta crystal should be as small as possible. For the selection of shell materials, CeO_2 may be one of the most suitable metal oxides owing to its outstanding oxygen storage and oxidation-reduction properties, which has been extensively used in various catalytic reactions [29–32]. Furthermore, NH_3 -SCR is also an acid catalysis reaction. The thicker of the coated oxide film, the weaker of the catalyst acidity. Thus, the suitable thickness of CeO_2 oxide film is of importance for high NH_3 -SCR activity.

Herein, a core–shell structural deNO_x catalyst, nano-size Beta supporting MoO_x and FeO_x bimetallic NPs as the core and CeO_2 thin film as sheaths, was demonstrated an excellent catalytic performances and high stability for H_2O and SO_2 -tolerance. In this design, CeO_2 sheath not only restrain the formation of ammonium nitrate and sulfate species blocking the active iron sites but also prevents from the generation of iron sulfate. Moreover, CeO_2 sheath can provide an effective barrier to suppress the migration and agglomeration of active metal oxide NPs during the deNO_x process. The catalysts show the high stability and SO_2 -tolerance. Thus, the excellent catalytic performances are obtained.

2. Experimental

2.1. Preparation of materials

The preparation process of MoFe/Beta@CeO_2 core–shell structure includes three steps as illustrated in Scheme 1. The first step involved the preparation of nano-size of HBeta crystals. The second one referred to the supporting of MoO_x and FeO_x NPs. Then, the Beta loaded with metal oxide NPs were then used as the support for the coating of CeO_2 sheaths.

Nano-size Beta ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$) crystals were synthesized by the following chemical composition: 1.4 Na_2O : 18 $(\text{TEA})_2\text{O}$: 1 Al_2O_3 : 100 SiO_2 : 1180 H_2O . A certain amount of tetraethylammonium hydroxide (TEAOH, 25 wt%), deionized water, silica sol (40 wt%), aluminum isopropoxide (98%) and sodium hydroxide ($>96\%$) were mixed under vigorous stirring for 24 h and then the gel was sealed into an autoclave and hydrothermal treatment at 100°C for 3 days. The product was obtained by washed with deionized water for more than three times, dried in air and calcined at

550°C for 6 h to get Na-Beta. H-Beta was obtained by treating Na-Beta with 0.1 mol/L NH_4NO_3 at 80°C for 8 h under vigorous stirring, then the H-Beta was dried in air and calcined at 450°C for 3 h.

MoFe/Beta catalyst was synthesized by an improved incipient wetness impregnation method using the above nano-size H-Beta zeolite as the catalyst support. In a typical synthesis, 1 g H-Beta powders was mixed with required amounts of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.18 g) and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (0.006 g) solution and bath ultrasounded in an ultrasound generator (70 W) for 4 h at room temperature, then evaporated water and dried in air followed by calcined at 550°C for 4 h. The obtained nanocomposites are denoted as MoFe/Beta .

For MoFe/Beta@CeO_2 core–shell catalyst, 100 mg of as-prepared MoFe/Beta nanocomposite was dispersed in a 100 mL mixed solution of water/ethanol ($v/v = 1$), then, 1 g polyvinylpyrrolidone (PVP) powder was added in the above solution and stirred until completely dissolved. Subsequently, 0.08 g $\text{Ce}(\text{NO}_3)_3$ and 0.06 g of hexamethylenetetramine were added in turn, and continued to stir and reflux for 2 h at 60°C . The product was obtained by centrifugation, washed with deionized water and ethanol, dried in air, followed by calcination in an inert environment at 500°C for 3 h. The final product was denoted as MoFe/Beta@CeO_2 .

For comparison, CeMoFe/Beta with the same Ce content as MoFe/Beta@CeO_2 core–shell catalyst was prepared by a conventional incipient wetness impregnation method. Pure CeO_2 NPs was synthesized as follows: 100 mg $\text{Ce}(\text{NO}_3)_3$ was dissolved in 100 mL mixed solution of water/ethanol ($v/v = 1$), and then 1 g PVP powder and 0.06 g HMT were introduced in turn. The mixture was heated to 60°C and refluxed at this temperature for 2 h before being cooled down to room temperature. The final product was obtained by centrifugation, washed with deionized water and ethanol, dried in air. Finally, the product was calcined in an inert environment at 500°C for 3 h.

Cu/SAPO-34 was synthesized by the following two-step ion-exchange (IE) process. H-SAPO-34 was prepared according to the procedure described in Ref [33]. First, an IE step was employed using an excess amount of 0.1 mol/L NH_4NO_3 at 50°C for 5 h to generate $\text{NH}_4\text{/SAPO-34}$. Subsequently, centrifugation separation and washing cycles were applied. Then, $\text{NH}_4\text{/SAPO-34}$ was further exchanged with 0.01 mol/L $\text{Cu}(\text{OAc})_2$ at 50°C for 1 h to generate the resulting Cu/SAPO-34 (~ 2.0 wt% Cu). Finally, the as-synthesized Cu/SAPO-34 was separated, washed and dried at 110°C , and then calcined at 550°C for 4 h.

2.2. Characterization of catalysts

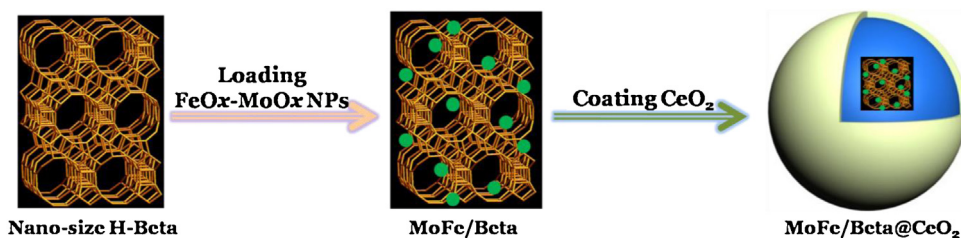
High resolution transmission electron microscopy (HRTEM) micrographs were conducted on a Tecnai G2 F20 electron microscope equipped with a field emission source operating at 200 kV. The elemental local, mapping and line-scanning analyses were collected by energy dispersive spectroscopy (EDS) using a Tecnai F20 electron microscope.

Scanning electron microscopy (SEM) measurements were obtained on a FEI Quanta 200F instruments with the working voltages of 5 kV.

Powder X-ray diffraction (XRD) pattern was performed on a Bruker D8 Advance diffractometer equipped with $\text{Cu K}\alpha$ radiation in the 2θ range of $5\text{--}70^\circ$ and scanning rate of $2^\circ/\text{min}$.

N_2 adsorption-desorption isotherms were recorded with a Micromeritics TriStar II 3020 porosimetry analyzer at 77 K .

X-ray photoelectron spectroscopy (XPS) spectra were collected on a PerkinElmer PHI-1600 ESCA spectrometer equipped with $\text{Mg K}\alpha$ ($h\nu = 1253.6\text{ eV}$) radiation. The binding energies were calibrated using C 1s peak of contaminant carbon ($\text{BE} = 284.6\text{ eV}$) as an internal standard. Deconvolution of Fe 2p, Mo 3d, O 1s and Ce 3d peak of catalysts was performed by using origin 7.0 software.



Scheme 1. Schematic illustration of the formation of MoFe/Beta@CeO₂ core-shell catalyst.

X-ray absorption near edge structure (XANES) of Fe L₃-edge spectra were recorded at Beamline 9-BM of Advanced Photon Source (APS), Argonne National Laboratory. The monochromator was double-crystal Si (111), and the XANES spectra were collected in fluorescence mode with a Si DRIFT 4-element detector (Vortex). Harmonics were rejected using of an Rh-coated flat mirror in the experimental station.

The element content of as-prepared materials was determined by a Varian 715-ES inductively coupled plasma-atomic emission spectrometer (ICP-AES).

Temperature-programmed desorption of ammonia (NH₃-TPD) measurements were conducted on a conventional flow apparatus. Prior to each test, 0.1 g of the catalyst was purged by a flowing N₂ (40 mL/min) at 600 °C for 30 min, and then the sample was cooled down to 100 °C. Subsequently, ammonia was adsorbed at this temperature for 30 min to ensure the sufficient adsorption of NH₃. Before desorption, the sample was purged by a flowing He stream at 100 °C for 1 h to remove excessive and physically adsorbed NH₃. Finally, the sample was heated from 100 to 500 °C at a rate of 10 °C/min in a pure N₂ (40 mL/min) flow and desorption pattern was recorded.

Temperature programmed reduction of hydrogen (H₂-TPR) experiment was conducted on a Chemisorb2720 TPx chemisorption analyzer. Prior to reduction, 50 mg of the catalyst was purged by a flowing N₂ (40 mL/min) at 600 °C for 30 min, and then the sample was cooled down to 60 °C in a N₂ flow. The temperature programmed reduction process was performed in flow of 10% H₂/N₂ (40 mL/min) up to 900 °C at a rate of 10 °C/min.

In-situ DRIFTS experiments were carried out on an FTIR spectrometer equipped with an MCT/A detector and a ZnSe window. The catalyst (about 0.1 g) was loaded in a Harrick IR cell and heated to 500 °C under N₂ purging at a total flow rate of 100 mL/min for 1 h to remove adsorbed impurities. A background spectrum was collected under a flowing N₂ atmosphere and was subtracted from the sample spectra. DRIFTS were recorded by accumulating 32 scans with a resolution of 4 cm⁻¹.

2.3. Activity evaluation

NH₃-SCR activity of the catalysts was evaluated on a fixed-bed micro-reactor operated in a steady flow mode. The typical reaction condition was as follows: [NH₃] = [NO] = 500 ppm, [SO₂] = 100 ppm, [O₂] = 3 vol%, 10% H₂O, N₂ balance and 500 mL/min total gas flow rate. 0.4 g catalyst (40–60 mesh) was employed. Therefore, the employed gas hourly space velocity (GHSV) was about 50,000 h⁻¹ for each activity test. The concentration of NO_x (NO_x = NO + NO₂) in the inlet and outlet gas at steady-state was measured using a flue gas analyzer (Model-4000VM, SIGNAL international Ltd., UK), and NH₃ and N₂O was monitored by a NEXUS 670-FTIR spectrometer. The NO_x conversion and N₂ selectivity were calculated using the following equations:

$$\text{NO}_x \text{ conversion} = \frac{[\text{NO}_x]_{\text{inlet}} - [\text{NO}_x]_{\text{outlet}}}{[\text{NO}_x]_{\text{inlet}}} \times 100\% \quad (1)$$

$$\text{N}_2 \text{ Selectivity} = \left(1 - \frac{2[\text{N}_2\text{O}]_{\text{outlet}}}{[\text{NO}_x]_{\text{inlet}} + [\text{NH}_3]_{\text{inlet}} - [\text{NO}_x]_{\text{outlet}} - [\text{NH}_3]_{\text{outlet}}} \right) \times 100\% \quad (2)$$

3. Results and discussion

3.1. TEM results

The morphology and shell structure of the as-prepared MoFe/Beta@CeO₂ was investigated by TEM and HRTEM combined with EDS elemental mapping and line analyses. As exhibited in Fig. 1a, through the self-assembly method, the outer surface of MoFe/Beta@CeO₂ was successfully covered by a thin metal oxides “layer”. As shown in Fig. 1b, HRTEM image shows that the shell-thickness is around 10 nm. Moreover, the property of the shell was further analyzed by selected-area electron diffraction, and the corresponding SAED pattern reveal the diffraction spots from (111), (200), (220), (311), which is attributed to CeO₂ fluorite crystalline features (Fig. 1c). Furthermore, the STEM image of a single MoFe/Beta@CeO₂ microsphere combined with EDX elemental mapping and line scanning analyses (Fig. 1e–h), clearly reveals the core–shell structure of MoFe/Beta@CeO₂. Therefore, as expected, the core–shell structure of MoFe/Beta@CeO₂ has been successfully prepared by this simple self-assembly method.

3.2. SEM results

SEM was performed to further insight into the change of the morphology of sample before and after coated by CeO₂ shell and the results are elucidated in Fig. 2. It was obviously noted that MoFe/Beta (Fig. 2a) is composed of egg-like aggregates with diameters around 100 nm, and that the surface of the catalyst is rough and decorated with numerous metal oxide NPs. By contrast, the surface of MoFe/Beta@CeO₂ becomes rougher after CeO₂ coating. EDS elemental analysis for MoFe/Beta@CeO₂ (Fig. 2b) shows that the content of Ce is 12.54 wt%. Fig. 2c shows HAADF-STEM images of MoFe/Beta@CeO₂ together with the elemental mapping images for Si, Al, O, Fe, Mo and Ce. From the elemental mapping image of Mo and Fe, it is clearly seen that Mo, Fe and Ce species are highly dispersed on the supports.

3.3. XRD results

In order to determine the phases and chemical compositions on MoFe/Beta@CeO₂, CeMoFe/Beta, MoFe/Beta and pure CeO₂, XRD detection was carried out, and the results are demonstrated in Fig. 3. For MoFe/Beta@CeO₂ (Fig. 3a), the diffraction peaks at 2θ = 7.6, 14.7 and 22.4° can be ascribed to the characteristic reflections of Beta [18]. While the weak diffraction peaks at 2θ = 28.6 and 33.0° can be indexed to the diffraction peaks of CeO₂ with the fcc fluorite structure [34,35]. Moreover, the diffraction peaks intensity corresponding to Beta zeolite remarkably decreases due to the modification of CeO₂ compared with MoFe/Beta, in agreement with its core (MoFe/Beta)@shell (CeO₂) nanostructure [36]. CeMoFe/Beta (Fig. 3b) exhibits similar diffraction peaks with

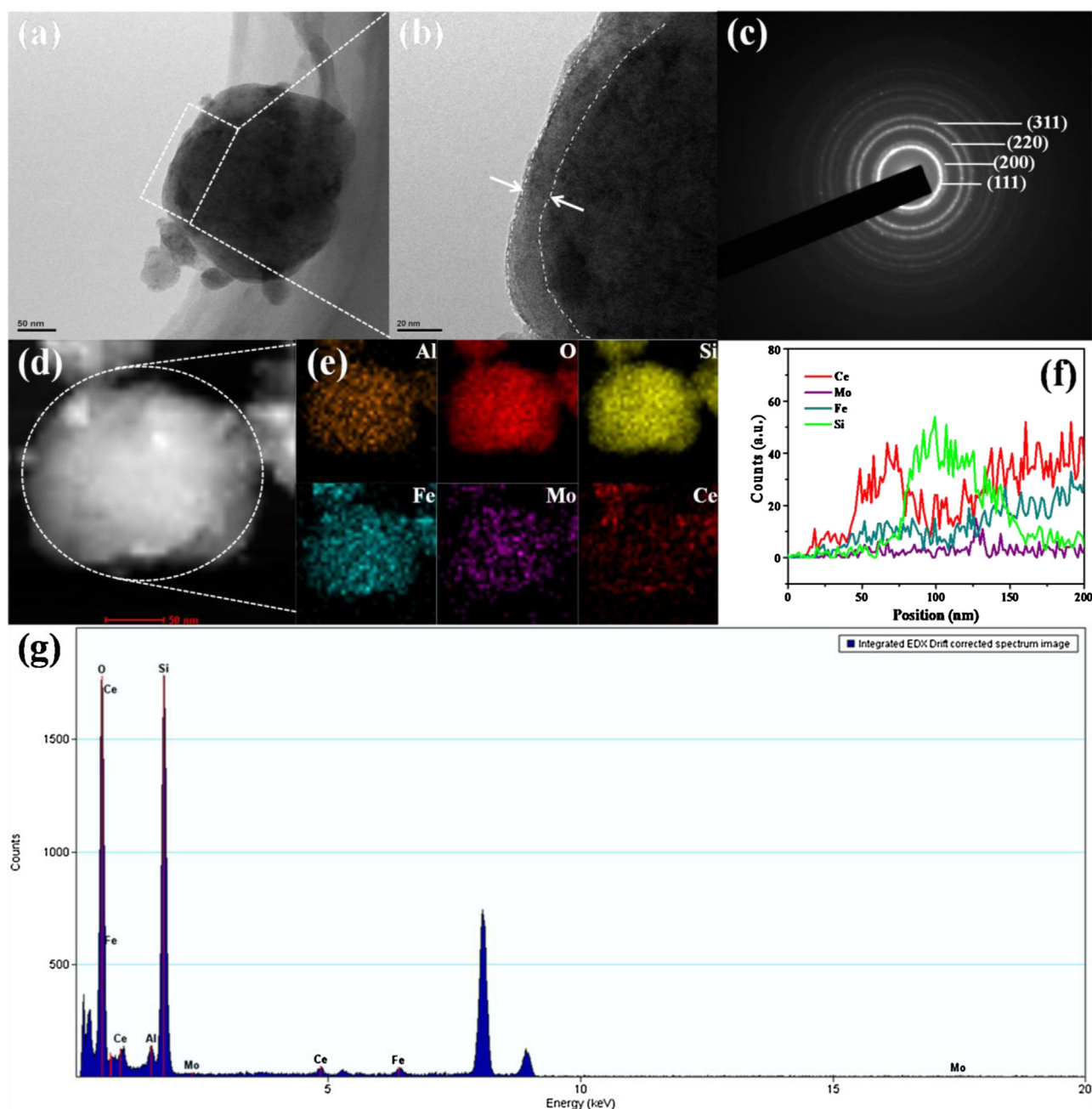


Fig. 1. (a) TEM image of MoFe/Beta@CeO₂ (b) HRTEM image of MoFe/Beta@CeO₂ (c) the SAED pattern of MoFe/Beta@CeO₂ (d) the STEM image of a single MoFe/Beta@CeO₂ microsphere; (e) the mapping elemental analyses for MoFe/Beta@CeO₂ (f) the line scanning of a typical particle and (g) EDS data of the single MoFe/Beta@CeO₂ microsphere.

MoFe/Beta@CeO₂ core–shell catalyst. The obvious differences are that the intensity of the characteristic diffraction peaks ascribed to Beta grows stronger, and several new peaks ascribed to CeO₂ appear, indicating that CeO₂ NPs distributed more homogeneously on MoFe/Beta@CeO₂ than on CeMoFe/Beta, which may be beneficial to the selective catalytic reduction of NO.

3.4. N₂ adsorption–desorption results

N₂ adsorption–desorption was carried out to investigate the change of the porous structure and specific surface area before and after coating with CeO₂ layers, and the results are shown in Fig. 4. It can be seen that the samples of MoFe/Beta@CeO₂, CeMoFe/Beta and MoFe/Beta are type-I isotherm, characteristic microporous materials [37]. While CeO₂ exhibits type-IV isotherms and typi-

Table 1

Surface area and pore volume of catalysts.

Samples	A_{BET}^a (m ² /g)	V_t^b (mL/g)	A_{Ext}^a (m ² /g)	V_{Meso}
MoFe/Beta@CeO ₂	402.0	0.251	134.9	0.140
CeMoFe/Beta	385.1	0.201	112.4	0.083
MoFe/Beta	362.7	0.203	131.3	0.107
CeO ₂	95.4	0.294	48.2	0.285

^a Calculated by BET method.

^b Calculated by *t*-plot method.

cal H₂ hysteresis loops, reflecting the mesoporous structure of the catalyst. Their BET surface areas and pore volumes are summarized in Table 1. The specific surface area (A_{BET}) and pore volume (V_t) of MoFe/Beta@CeO₂ is 402.0 m²/g and 0.251 mL/g, respectively. It is obviously larger than that of MoFe/Beta (362.7 m²/g

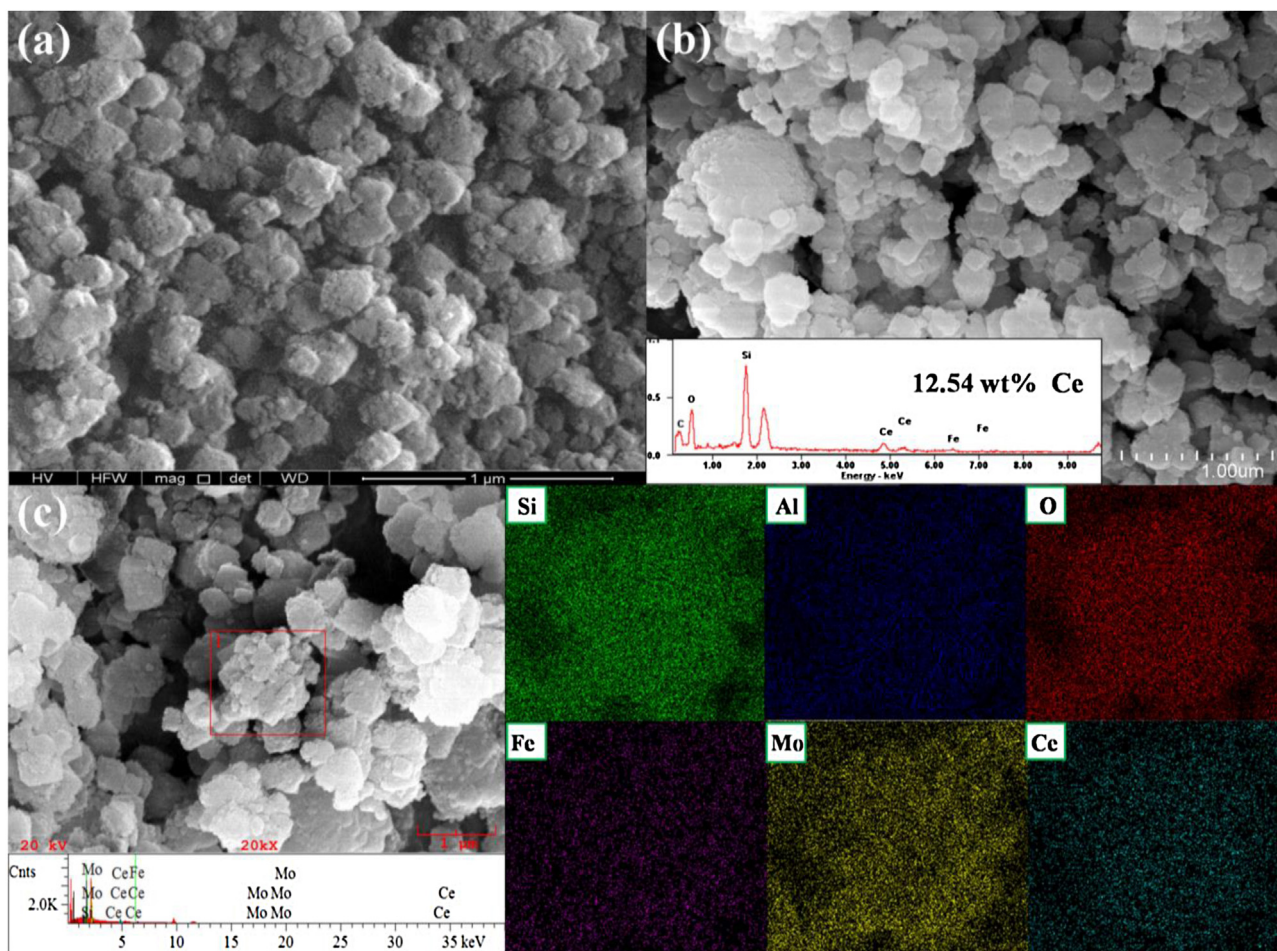


Fig. 2. SEM images of the catalysts: (a) MoFe/Beta and (b) MoFe/Beta@CeO₂ and (c) HAADF-STEM image and EDS elemental analyses for MoFe/Beta@CeO₂.

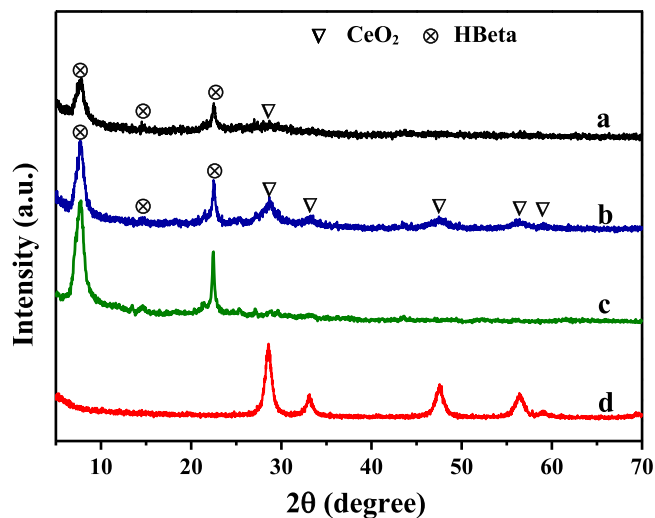


Fig. 3. XRD patterns of the catalysts: (a) MoFe/Beta@CeO₂ (b) CeMoFe/Beta (c) MoFe/Beta and (d) CeO₂.

and 0.203 mL/g), which may be due to the formation of mesopores resulting from the coating with CeO₂ layer. The mesoporous feature of CeO₂ shells is beneficial to the transport of reactant molecules and necessary to improve the accessibility of reactants to catalytic active sites, which is evidenced by the catalytic performance of MoFe/Beta@CeO₂ below. In addition, it's noted that CeMoFe/Beta

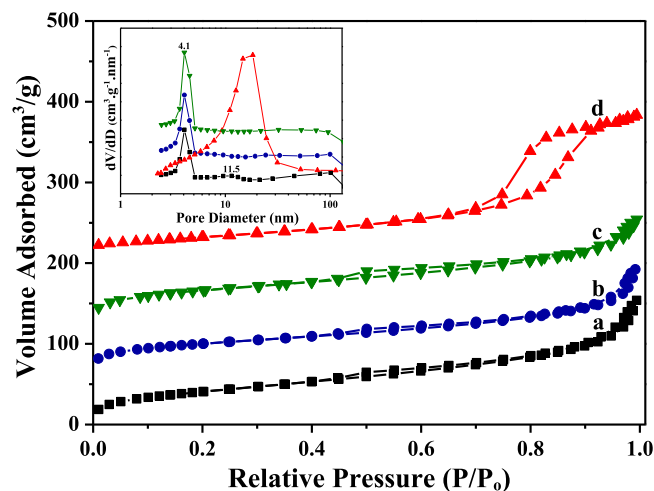


Fig. 4. (A) Nitrogen adsorption-desorption isotherms and (B) the size distribution curves of the catalysts: (a) MoFe/Beta@CeO₂ and (b) CeMoFe/Beta (c) MoFe/Beta and (d) CeO₂.

exhibit a similar pore volume with MoFe/Beta. While the external surface area (A_{Ext}) and mesoporous pore volume (V_{Meso}) are smaller than those of MoFe/Beta due to the deposition of CeO₂. The pore size distribution which is calculated with the BJH model is exhibited in Fig. 4 (inset). It can be observed that all of MoFe/Beta@CeO₂, CeMoFe/Beta and MoFe/Beta catalysts show similar pore distribu-

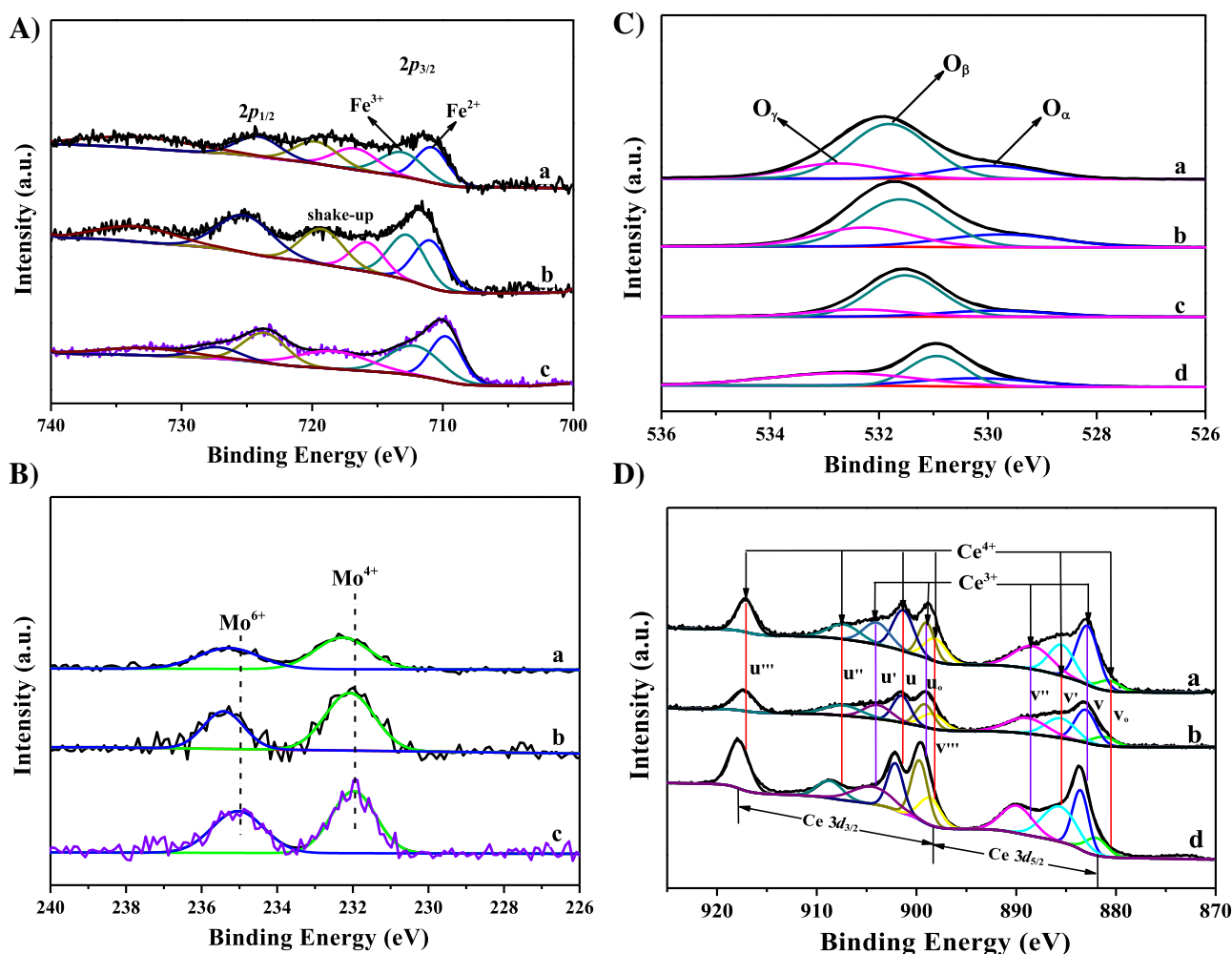


Fig. 5. XPS spectra of (A) Fe 2p, (B) Mo 3d (C) O 1s and (D) Ce 3d of the catalysts: (a) MoFe/Beta@CeO₂ (b) CeMoFe/Beta (c) MoFe/Beta (d) CeO₂.

tion. It reveals that the coating of CeO₂ shell didn't damage the initial structure of MoFe/Beta, which is consistent with XRD results. In addition, a weak pore size around at 11.5 nm is observed over MoFe/Beta@CeO₂ (Fig. 4 (inset)), which should contribute to the enhancement of specific surface area.

3.5. XPS results

XPS technique was used to characterize the chemical state and the atomic concentrations of catalyst surface component. Fig. 5 shows XPS spectra of Fe 2p, Mo 3d, O 1s and Ce 3d, and the corresponding surface atomic concentrations and the relative atomic concentration ratios are summarized in Table 2. As for MoFe/Beta@CeO₂, the surface concentration of Fe (1.14%) and Mo (0.21%) are found to be lower than those of CeMoFe/Beta (1.25% & 0.29%) and MoFe/Beta (1.34% & 0.33%). It indicates that Fe and Mo are within the cerium oxides layers, thus the corresponding photoelectrons intensity is lower. It is in good conformity to TEM analysis. Fig. 5A shows XPS results of Fe 2p_{3/2} for MoFe/Beta@CeO₂ and MoFe/Beta catalysts. Peaks located near 712.5 and 710 eV can be assigned to Fe³⁺ and Fe²⁺, respectively [38,39]. It indicates that the iron in our samples is present both as Fe²⁺ and Fe³⁺. The results from deconvolution are presented in Table 2. It is noted that the surface Fe²⁺/Fe³⁺ ratio increases about 9.7% after coating CeO₂ shell. As is well known, Fe²⁺/Fe³⁺ redox-couples could promote the formation of oxygen vacancies and redox cycle. The more Fe²⁺, the easier to form oxygen vacancies, and the more advantageous to the

adsorption of oxygen on catalyst surface to form chemisorbed oxygen species. In addition, Fe 2p spectra of MoFe/Beta@CeO₂ move slightly to the higher binding energy, demonstrating an interaction between iron oxide species and CeO₂ layers.

As shown in Fig. 5B, XPS spectra of Mo 3d were fitted into two peaks centered at 232.0 and 235.0 eV, which are attributed to MoO₂ and MoO₃, respectively [40]. This result indicates that only Mo⁴⁺ and Mo⁶⁺ species are present on MoFe/Beta@CeO₂ and MoFe/Beta catalysts. Additionally, it can clearly be seen that Mo 3d spectra of MoFe/Beta@CeO₂ also shift slightly to higher binding energy.

Fig. 5C presents O 1s XPS spectra of MoFe/Beta@CeO₂, CeMoFe/Beta, MoFe/Beta and pure CeO₂, which were fitted into three peaks corresponding to the lattice oxygen O_α (529.5–530.2 eV), chemisorbed oxygen O_β (531.4–531.7 eV) and hydroxyl groups O_γ (532.4–532.9 eV), respectively [41,42]. It's noted that a distinct increase of the intensities corresponding to O_β and O_γ have been observed after coating by CeO₂. It can be clearly observed from Table 2 that the molar concentration of O_β on MoFe/Beta@CeO₂ (59.8%) is slightly higher than that on CeMoFe/Beta (57.6%) and MoFe/Beta (54.9%). It's been accepted that the O_β is the most active oxygen species and plays an important role in the redox reaction, and may contribute to the excellent NH₃-SCR performance of MoFe/Beta@CeO₂. In addition, Kwon et al. [23] found that the high ratio of surface chemisorbed oxygen was conducive to increase catalytic activity and SO₂ resistance. Furthermore, it is important to note that the amount of O_γ increases from 21.7% to 23.5% after CeO₂ sheath coating. It indicates the increase of

Table 2

The surface atomic concentrations of Fe, Mo, Ce, O and the relative concentration ratios.

Catalyst	surface atomic concentrations				relative concentration ratios		
	Fe	Mo	O	Ce	Fe ²⁺ /Fe	O _γ /O	O _β /O
MoFe/Beta@CeO ₂	1.14%	0.21%	38.69%	2.99%	58.4%	23.5%	59.8%
CeMoFe/Beta	1.25%	0.29%	32.26%	0.72%	48.6%	24.7%	57.6%
MoFe/Beta	1.34%	0.33%	28.34%		48.7%	21.7%	54.9%
CeO ₂			87.49%	12.51%		39.8%	38.9%

hydroxyl groups, which could serve as Brønsted acid sites to adsorb NH₃ and form NH₄⁺ and then react with NO₂ adsorbed nearby to produce N₂ and H₂O during NH₃-SCR process. Thus, it can enhance NH₃-SCR performance. The last but not the least, it is noteworthy that the O 1s peak for MoFe/Beta@CeO₂ shifts to a higher binding energy compared with MoFe/Beta due to the interaction between the lattice oxygen and metal atoms, which may be conducive to the oxidation of NO to NO₂ in the SCR reaction [23,43]. Therefore, it facilitates the improvement of the low-temperature NH₃-SCR performance.

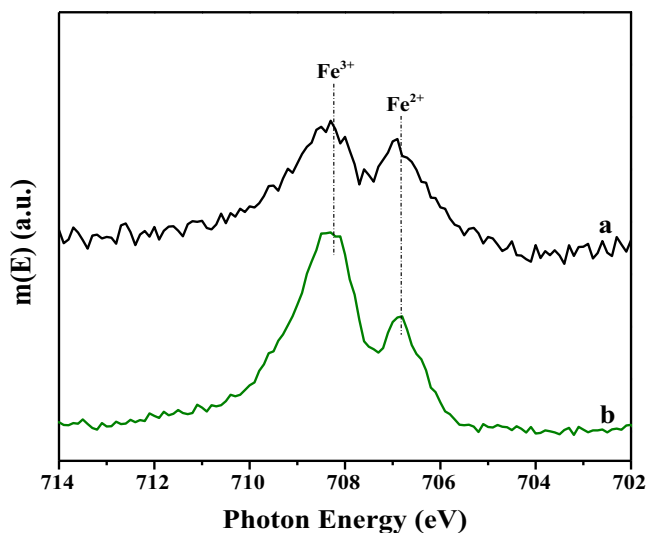
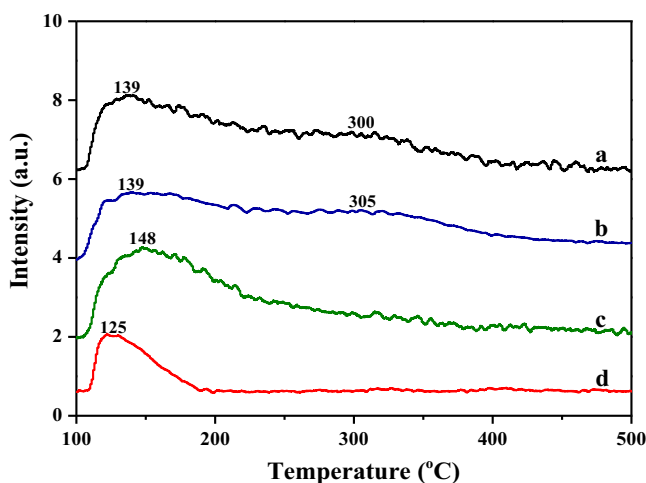
Fig. 5D shows the Ce 3d XPS spectrum of MoFe/Beta@CeO₂, CeMoFe/Beta and pure CeO₂, which is split into ten peaks arising from Ce⁴⁺ (u''', u'', u, v''', v' and v₀) and Ce³⁺ (u', u₀, v' and v) contributions [27,28]. It indicates that the coexistence of Ce³⁺ and Ce⁴⁺ in all of the three samples. In addition, Ce 3d_{3/2} and Ce 3d_{5/2} peaks of MoFe/Beta@CeO₂ shift slightly to the lower binding energies compared with the pristine CeO₂, which can be ascribed to the interface effects between the core and shell. It indicates that there is a strong interaction between CeO₂ shell and MoFe/Beta core, which may play a synergistic role in the NH₃-SCR reaction.

3.6. XANES results

In order to further explore the effect of the coating of CeO₂ shell on chemical state and coordination state of iron species, XANES experiment was performed in total electron yield mode. Prior to each test, the samples were mixed with graphite powders to increase electric conductivity and minimize charging effect. The Fe L₃-edge XANES spectra of MoFe/Beta@CeO₂ and MoFe/Beta are shown in Fig. 6. Two distinct absorption peaks are observed at 706.8 eV (A₁) and 708.8 eV (A₂) due to the interplay of crystal field, spin-orbital and electronic interaction [44], which is consistent with the results reported by Yang, et al. [45]. Based on the charge transfer multiplet theory [46], the peaks at 706.8 eV (A₁) and 708.8 eV (A₂) correspond to the 2p_{3/2} → 3d electron transition for Fe²⁺ and Fe³⁺, respectively. Moreover, the absorption bands corresponding to Fe²⁺ and Fe³⁺ shift slightly to the higher photon energy, confirming the existence of electronic inductive effect between the coating of CeO₂ shell and MoFe/Beta core. Furthermore, the intensity ratios of A₁/(A₁ + A₂) for MoFe/Beta@CeO₂ and MoFe/Beta are calculated to be 0.47 and 0.36, respectively. The results reveal that in the two samples there coexist in comparable quantity both Fe²⁺ and Fe³⁺ states, and more importantly, MoFe/Beta coated by CeO₂ shell has significantly higher fraction of Fe²⁺ than the uncoated one, which agrees well with the XPS results. Combined with XPS results, it demonstrates that the coating of CeO₂ shell significantly influence the ratio of Fe²⁺/Fe³⁺ on MoFe/Beta@CeO₂ catalyst, and then the NH₃-SCR performance may be regulated.

3.7. NH₃-TPD results

It's widely accepted that the adsorption and activation of NH₃ molecule on the acid sites of catalyst surface are a primary process in NH₃-SCR reaction. Therefore, NH₃-TPD profiles were carried to investigate the effect of CeO₂ shell on the acidity of the catalysts, and the results are shown in Fig. 7. Both MoFe/Beta and CeO₂ cat-

**Fig. 6.** XANES spectra of the catalysts: (a) MoFe/Beta@CeO₂ (b) MoFe/Beta.**Fig. 7.** NH₃-TPD profiles of the catalysts: (a) MoFe/Beta@CeO₂ (b) CeMoFe/Beta (c) MoFe/Beta (d) CeO₂.

alysts show one desorption peak at 148 and 125 °C, respectively. Whereas, for MoFe/Beta@CeO₂ core-shell catalyst, two distinct NH₃ desorption peaks are observed at 139 and 300 °C, which can be attributed to physisorbed NH₃ and/or ammonium species adsorbed at the weak acid sites and NH₃ adsorbed at the strong acid sites, respectively [47]. It has been demonstrated that the temperature of desorption peak reflects the acid strength of the catalyst, while the peak area represents the acid amount [27,48]. Consequently, it is evident that the acid amount and acid strength of strong acid sites have been enhanced after CeO₂ coating, which may be beneficial for the NH₃-SCR reaction. Additionally, it's also noted that the acid amount and acid strength of weak acid sites decrease distinctly due to CeO₂ coating. It's well known that NH₃-SCR reaction is an acid

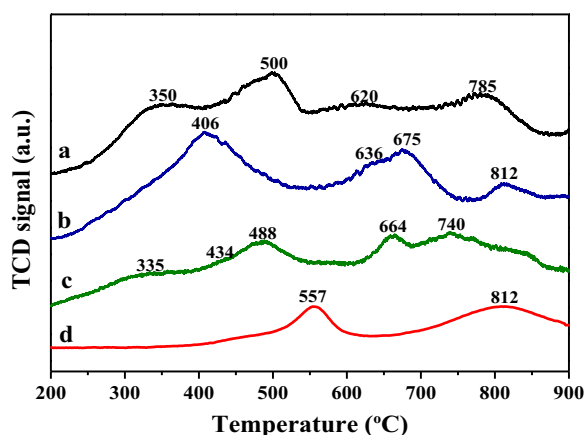


Fig. 8. H_2 -TPR profiles of the catalysts: (a) MoFe/Beta@CeO₂ (b) CeMoFe/Beta (c) MoFe/Beta (d) CeO₂.

catalysis and redox reaction. Although the acidity of the catalyst is not a crucial factor for high NH_3 -SCR activity, proper amount of it can promote SCR activity [49].

3.8. H_2 -TPR results

The redox property of catalyst plays a vitally important role in the catalytic process of NH_3 -SCR of NO. H_2 -TPR was employed to study the change of reducibility of the catalysts before and after coating by CeO₂ sheaths, and the results are displayed in Fig. 8. For CeO₂, two broad reduction peaks are observed. The first one centered at 557 °C is ascribed to the reduction of surface capping oxygen, while the second one centered at 812 °C is assigned to bulk oxygen of ceria [50]. H_2 -TPR profile of MoFe/Beta presents five reduction peaks at 335, 434, 488, 664 and 740 °C, which can be attributed to the reduction of Fe₂O₃ to Fe₃O₄, highly dispersed Mo species, Fe₃O₄ to Fe, Fe₃O₄ to FeO and FeO to Fe, respectively [4,51]. By contrast, after coating by CeO₂ shell, the reduction peak attributed to iron oxide and molybdenum oxide species shifted slightly to the higher temperature, which may be attributed to the interaction of CeO₂ sheaths with iron oxide and molybdenum oxide species. It agrees well with the results of XPS analysis. Additionally, it is worth noting that the peak corresponds to the reduction of iron oxide species becomes broader and stronger. It's generally accepted that the area of reduction peak is positively related to the amount of active species. Therefore, it demonstrates the increase of the iron oxide species that can be reduced or the increase of redox property of cerium oxide NPs, all of which are beneficial to the enhancement of NH_3 -SCR of NO. Furthermore, compared with MoFe/Beta@CeO₂ core-shell catalyst, CeMoFe/Beta exhibits a higher temperature corresponding to the reduction of iron oxide species. Combined with the above observations, it can be deduced that the interaction between iron oxide, molybdenum oxide and CeO₂ shells plays a synergistic role in the reducibility of the MoFe/Beta@CeO₂ core-shell catalysts, which could promote the activity of the catalyst in NH_3 -SCR reaction.

3.9. Catalytic performance results

In practical use, SO₂ is an important factor in the effluent gases from diesel engines influencing SCR activity over the catalysts. The trace amounts of SO₂ can result in the decrease of the catalytic performance [52]. Fig. 9A shows the NO_x conversion of MoFe/Beta@CeO₂, CeMoFe/Beta, MoFe/Beta, CeO₂ and Cu/SAPO-34 catalysts in the presence of 100 ppm SO₂ in the range of 100–600 °C under the GHSV of 50,000 h⁻¹. It can be observed that the NO_x

conversion changes with the increase of reaction temperature. For pure CeO₂, the maximum NO_x conversion is only 73.5% at 400 °C in the whole temperature range. MoFe/Beta@CeO₂ exhibits a higher low-temperature NO_x conversion and a wider operation temperature window than the other catalysts. The NO_x conversion is above 90% in the range of 225–600 °C over MoFe/Beta@CeO₂ catalyst. While for MoFe/Beta, the NO_x conversion reaches to 90% nearly at 300 °C and dramatically decreases when the reaction temperature is beyond 500 °C. It may be due to the migration and agglomeration of the metal oxides at high temperature, leading to the deactivation of catalysts. By contrast, MoFe/Beta@CeO₂ catalyst exhibits more robust at corresponding conditions. In addition, it can also be seen that the low-temperature NH_3 -SCR performance of CeMoFe/Beta was improved to some extent compared to MoFe/Beta. However, the NO_x conversion gradually declines when the reaction temperature is over 450 °C, which may be due to the presence of bigger CeO₂ NPs (as shown in Fig. 3b), aggravating the unselective oxidation of NH_3 . Cu/SAPO-34, a representative NH_3 -SCR zeolite catalyst, was also conducted for the purpose of comparison. It can be seen that Cu/SAPO-34 catalyst exhibited a relatively lower NO_x conversion compared with MoFe/Beta in the whole temperature range, revealing that MoFe/Beta exhibits better SO₂-tolerance than Cu/SAPO-34 catalyst. According to the above observations, it can be concluded that CeO₂ sheaths have effectively suppressed the formation of ammonium sulfate species blocking the active sites and prevented SO₂ from poisoning active phases over MoFe/Beta@CeO₂ catalyst at low temperature. The migration and aggregation of the active metal oxides are prevented at high temperature (>450 °C). Thus, the stability of the catalyst is enhanced. The excellently catalytic activity of MoFe/Beta@CeO₂ catalyst could be ascribed to the core-shell structure of CeO₂ coating MoFe/Beta.

The N₂ selectivity is a crucial role in evaluating the catalytic activity of SCR catalyst. As shown in Fig. 9B, nearly 100% N₂ selectivity was obtained over MoFe/Beta@CeO₂, CeMoFe/Beta, MoFe/Beta and Cu/SAPO-34 catalysts in the whole temperature range of 100–600 °C. However, in the case of CeO₂, the N₂ selectivity remarkably decreased as reaction temperature is above 300 °C, which should be due to the unselective catalytic oxidation of NH_3 to N₂O and/or NO.

As an important indicator of evaluation the performance of catalysis, the catalytic stability of the catalysts before and after CeO₂ coating is investigated. Fig. 9C shows the stability tests of the catalysts in the presence of 100 ppm SO₂ as a function of time at 300 °C. Surprisingly, it can be noted that the catalytic performance of MoFe/Beta@CeO₂ catalyst is barely affected by SO₂ in the feed gas, and the NO_x conversion over the catalyst still maintains at around 98% after 25 h tested, indicating the high resistance ability of MoFe/Beta@CeO₂ catalyst to SO₂ poisoning. For CeMoFe/Beta, the NO_x conversion gradually declines with the time on stream and decreases to about 6% after 25 h. In sharp contrast, the deNO_x activity of MoFe/Beta sharply drops within 4 h and decreases to 77% after 25 h. While for Cu/SAPO-34, it can be seen that NO_x conversion dramatically declines within 2 h and decreases to 62% after 4 h. SO₂ resulting in catalyst poisoning and deactivation derives from the following two aspects. On the one hand, the reaction of SO₂ and NH_3 generates ammonium sulfate species depositing on the catalyst surface and blocking the active sites of the catalyst surface, which can result in a gradual decrease of NO_x conversion. The deactivation of the catalyst resulted from this process is reversible. On the other hand, the active phases of the catalyst react with SO₂ to form stable sulfated species leading to a rapid decrease of NO_x conversion, which results in an irreversible deactivation [53]. Therefore, it can be concluded that compared to CeMoFe/Beta catalyst, MoFe/Beta@CeO₂ shows a remarkable resistance to SO₂ due to the protection of CeO₂ shell.

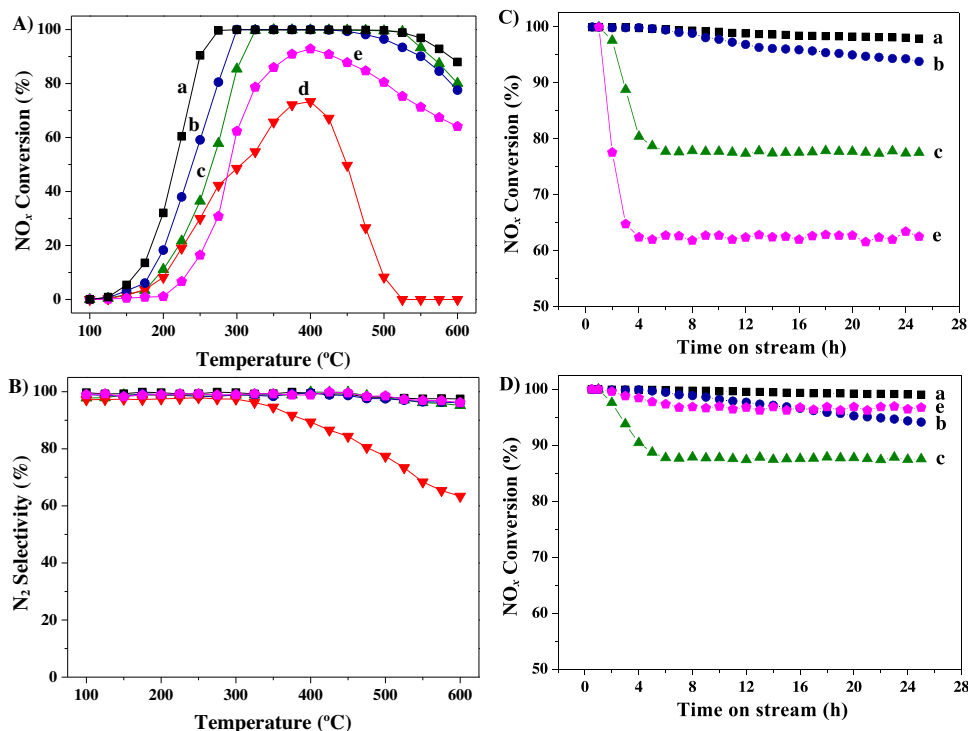


Fig. 9. (A) NO_x conversion and (B) N₂ selectivity in the presence of SO₂: (a) MoFe/Beta@CeO₂ (b) CeMoFe/Beta (c) MoFe/Beta (d) CeO₂ (e) Cu/SAPO-34 (C) Tests of SO₂ resistance and (D) Tests of H₂O resistance at 300 °C: (a) MoFe/Beta@CeO₂ (b) CeMoFe/Beta (c) MoFe/Beta (e) Cu/SAPO-34. Reaction conditions: [NO] = [NH₃] = 500 ppm, [SO₂] = 100 ppm, [O₂] = 3 vol%, [H₂O] = 10%, N₂ balance and GHSV = 50,000 h⁻¹.

The effect of H₂O on the SCR activity over MoFe/Beta@CeO₂, CeMoFe/Beta and MoFe/Beta as a function of time at 300 °C was also investigated, and the results were exhibited in Fig. 9D. It can be found that MoFe/Beta@CeO₂ catalyst exhibits the best NH₃-SCR performance with NO_x conversion above 99% in the whole test range in the presence of 10% H₂O. For MoFe/Beta, the NO_x conversion rapidly decreases to around 87% after 6 h, which may be due to the aggregation of active metals and/or the structure collapsed of support [54]. While for CeMoFe/Beta, the NO_x conversion is somewhat improved compared with MoFe/Beta catalyst and is still lower than MoFe/Beta@CeO₂. It indicates high H₂O resistance ability of MoFe/Beta@CeO₂ core-shell catalyst.

It was reported that the presence of SO₂ had a great effect on NO adsorption and oxidation in SCR reaction, which could form sulfate species ((NH₄)₂SO₄ and NH₄HSO₄) blocking the active sites for NO oxidation and then cut off the reaction pathway [6,55,56]. The in-situ DRIFTS spectra of co-adsorption of NO + O₂ over MoFe/Beta@CeO₂ and MoFe/Beta catalysts after SO₂ tolerance test at 200 °C are investigated and the results are displayed in Fig. 10. It can be noted from Fig. 10A that several distinct bands appear at 1612, 1390, 1355 and 1231 cm⁻¹ after 40 min of exposure, which are assigned to asymmetric stretching vibration of gaseous NO₂, *trans*-N₂O₂²⁻, linear nitrites and monodentate nitrate, respectively [57–59]. The intensity of these peaks gradually enhances with the time. According to the above observations, it can be inferred that the formation of NO₂ and nitrites species, to some degree, can account for the high deNO_x performance of MoFe/Beta@CeO₂ at the low temperature.

Fig. 10B exhibits the in-situ DRIFT spectra of NO + O₂ co-adsorption on MoFe/Beta catalyst, which is different from that of MoFe/Beta@CeO₂. Three distinct bands are observed at 1301, 1259 and 1199 cm⁻¹, which can be ascribed to monodentate nitrate, monodentate nitrite and bridging nitrate, respectively [43,47]. It has been accepted that the formation of nitrate species is unfavorable for the NH₃-SCR reaction, which is very stable and can cover the

active sites resulting in the decrease of NH₃-SCR performance [58]. Furthermore, it is important to note that the intensity of the band at 1612 cm⁻¹ ascribed to gaseous NO₂ is much lower than that of MoFe/Beta@CeO₂. According to the above observation, it from a side proves that CeO₂ shells have considerably suppressed the formation of sulfate species and ammonium nitrate blocking the active iron sites. Moreover, It also demonstrates that CeO₂ shell coating catalyst not only inhibit the formation of nitrate species from covering the active iron sites but also can promote the generation of nitrites species and NO₂ during NH₃-SCR, and then enhance the NH₃-SCR performance.

Combined with the above observations, it can be concluded that ceria-shell functions as a protective layer greatly enhanced the NH₃-SCR performance, thermal stability and SO₂/H₂O-tolerance of MoFe/Beta catalyst. The reasons may be as following: Firstly, owing to the presence of ceria-shell functions serving as a protective layer, SO₂ can't directly react with active component on MoFe/Beta@CeO₂ catalyst to produce inactive sulfate species. Therefore, the active iron sites were protected and then the low-temperature performance of MoFe/Beta@CeO₂ catalyst was enhanced. Secondly, because of the presence of strong interaction among the iron oxides, molybdenum oxides and CeO₂ shells (confirmed by XPS and H₂-TPR), CeO₂ shells can serve as an effective barrier to inhibit the active metal oxides nanoparticles from aggregating at high temperature. As a result, the coated catalyst with CeO₂ thin film shows an improved thermal stability. Finally, the formation of sulfated ceria species may increase the amount of surface active oxygen and surface hydroxyls, which is beneficial to improving the ability of NO oxidation to NO₂ and then promoting the "fast SCR" process during NH₃-SCR [6].

Presumably CeO₂ gradually transforms to Ce(SO₄)₂, but what happens when the transformation is complete? Indeed, this phenomenon would happen that CeO₂ gradually transforms to Ce(SO₄)₂ in the presence of SO₂, which has been reported by many researchers. But it is slightly different in this work. First of all,

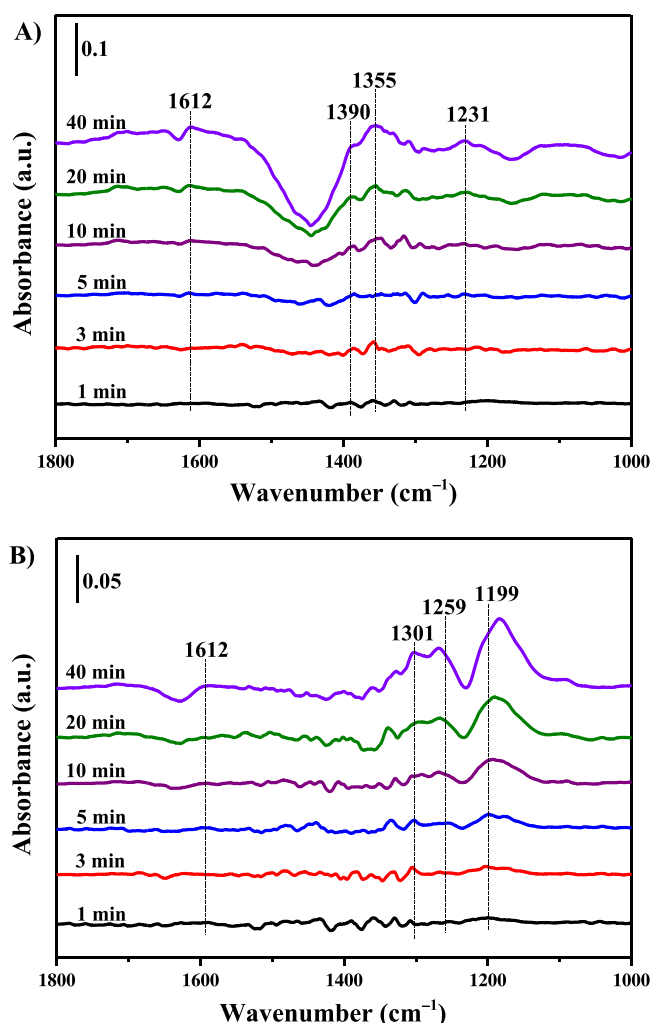


Fig. 10. In situ DRIFTS spectra of NO + O₂ adsorption on sulfated catalysts measured at 200 °C (A) MoFe/Beta@CeO₂ (B) MoFe/Beta.

MoFe/Beta@CeO₂ catalyst is protected by the outer CeO₂ shell, which is about 10 nm. Although, CeO₂ gradually transforms to Ce(SO₄)₂ and even completely transformation along with the process of SCR reaction, “CeO₂ shells” can still inhibit the ammonium nitrate and sulfate species (NH₄HSO₄) formed in this SCR process from depositing on the surface of catalyst and blocking the active iron sites over MoFe/Beta@CeO₂ catalyst, and then guaranteeing the reaction smoothly. What’s more, CeO₂ shells can still serve as an effective barrier to inhibit the active metal oxides nanoparticles from aggregating at high temperature. Therefore, the coated catalyst with CeO₂ thin film can show an improved thermal stability. The last but not the least, even though CeO₂ gradually transforms to Ce(SO₄)₂, on the one hand, the formation of Ce(SO₄)₂ could increase the amount of surface active oxygen species, and then promote the ability of NO oxidation to NO₂. On the other hand, the amount of surface hydroxyls due to the hydration of SO₄²⁻ may be increased, which could supply more Brønsted acid sites to adsorb NH₃ in the form of NH₄⁺. The both factors played significant roles in the good SO₂ durability of SCR catalyst. Certainly, as the CeO₂ shell completely transforms to Ce(SO₄)₂, SO₂ would gradually react with active component over MoFe/Beta@CeO₂ catalyst to generate inactive sulfate species, resulting in deactivation of the catalyst. In summary, it has to say that this work lays a foundation for guiding the development of highly active NH₃-SCR catalysts core-shell structure.

4. Conclusions

We have designed a new MoFe/Beta@CeO₂ core-shell catalyst with nano-size Beta supporting MoFe bimetallic oxides as the core and CeO₂ thin film as the shell. MoFe/Beta@CeO₂ catalyst exhibits higher catalytic performances, higher stability, H₂O and SO₂-tolerance than either pure CeO₂ or MoFe/Beta for NH₃-SCR reaction. The NO_x conversion is above 90% in the temperature range of 225–600 °C over MoFe/Beta@CeO₂ catalyst even if the reaction gases include 100 ppm SO₂. It can be ascribed to the interface effects between the core (MoFe/Beta) and shell (CeO₂).

The interface effects between the molybdenum oxide, iron oxide and CeO₂ sheaths have not only restrained the formation of ammonium sulfate and nitrate species from blocking the active sites but also prevented the generation of iron sulfate, leading to a high SO₂-tolerance. Moreover, CeO₂ shells have served as an effective barrier to suppress the migration and aggregation of active metal oxides and thus enhance the thermal stability. Furthermore, the CeO₂ shell coating catalyst not only can promote the formation of nitrites species but also strengthen the acidity of catalyst and promote NO oxidation to NO₂, which may be an important factor accounting for the high catalytic performances of MoFe/Beta@CeO₂ core-shell catalyst. Therefore, the present work lays a foundation for guiding the development of highly active NH₃-SCR catalysts and the design and application of core-shell catalysts.

Acknowledgements

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References

- [1] J.O. Barth, A. Jentys, J.A. Lercher, *Ind. Eng. Chem. Res.* 43 (2004) 3097–3104.
- [2] A. Boubnov, H.W.P. Carvalho, D.E. Doronkin, T. Guenter, E. Gallo, A.J. Atkins, C.R. Jacob, J.D. Grunwaldt, *J. Am. Chem. Soc.* 136 (2014) 13006–13015.
- [3] E. Garcia-Bordeje, J.L. Pinilla, M.J. Lazaro, R. Moliner, *Appl. Catal. B* 66 (2006) 281–287.
- [4] P. Balle, B. Geiger, S. Kureti, *Appl. Catal. B* 85 (2009) 109–119.
- [5] J.P. Dunn, P.R. Koppula, H.G. Stenger, I.E. Wachs, *Appl. Catal. B* 19 (1998) 103–117.
- [6] Y. Shu, T. Aikebaier, X. Quan, S. Chen, H. Yu, *Appl. Catal. B* 150 (2014) 630–635.
- [7] P. Szazama, B. Wichterlova, S. Sklenak, V.I. Parvulescu, N. Candu, G. Sadovska, J. Dedecsek, P. Klein, V. Pashkova, P. Stastny, *J. Catal.* 318 (2014) 22–33.
- [8] T. Zhang, J. Li, J. Liu, D. Wang, Z. Zhao, K. Cheng, J. Li, *AlChE J.* 61 (2015) 3825–3837.
- [9] S. Andonova, S. Tamm, C. Montreuil, C. Lambert, L. Olsson, *Appl. Catal. B* 180 (2016) 775–787.
- [10] T. Zhang, J. Liu, D. Wang, Z. Zhao, Y. Wei, K. Cheng, G. Jiang, A. Duan, *Appl. Catal. B* 148–149 (2014) 520–531.
- [11] R. Delahay, S. Kieger, N. Tanchoux, P. Trems, B. Coq, *Appl. Catal. B* 52 (2004) 251–257.
- [12] O. Mihai, C.R. Widyastuti, S. Andonova, K. Kamasamudram, J. Li, S.Y. Joshi, N.W. Currier, A. Yezerets, L. Olsson, *J. Catal.* 311 (2014) 170–181.
- [13] X. Zhang, Q. Shen, C. He, C. Ma, J. Cheng, L. Li, Z. Hao, *ACS Catal.* 2 (2012) 512–520.
- [14] P.J. Jodlowski, J. Kryca, A. Rogulska, B. Gil, M. Iwaniszyn, J. Lojewska, A. Kolodziej, *Chem. Eng. J.* 214 (2013) 319–326.
- [15] R. Foo, T. Vazhnova, D.B. Lukyanov, P. Millington, J. Collier, R. Rajaram, S. Golunski, *Appl. Catal. B* 162 (2015) 174–179.
- [16] K. Gora-Marek, K. Brylewska, K.A. Tarach, M. Rutkowska, M. Jablonska, M. Choi, L. Chmielarz, *Appl. Catal. B* 179 (2015) 589–598.
- [17] S. Shwan, L. Olsson, M. Skoglundh, J. Jansson, *AlChE J.* 61 (2015) 215–223.
- [18] S.Y. Jiang, R.X. Zhou, *Fuel Process. Technol.* 133 (2015) 220–226.
- [19] Y.J. Kim, H.J. Kwon, I. Heo, I.S. Nam, B.K. Cho, J.W. Choung, M.S. Cha, G.K. Yeo, *Appl. Catal. B* 126 (2012) 9–21.
- [20] J.D. Han, *Clean Technol.* 21 (2015) 153–163.
- [21] E.J.M. Hensen, P.J. Kooyman, Y. van der Meer, A.M. van der Kraan, V.H.J. de Beer, J.A.R. van Veen, R.A. van Santen, *J. Catal.* 199 (2001) 224–235.
- [22] Y.Y. Shu, R. Ohnishi, M. Ichikawa, *J. Catal.* 206 (2002) 134–142.
- [23] D.W. Kwon, K.H. Park, S.C. Hong, *Chem. Eng. J.* 284 (2016) 315–324.
- [24] R.G. Chaudhuri, S. Paria, *Chem. Rev.* 112 (2012) 2373–2433.

- [25] M.B. Gawande, A. Goswami, T. Asefa, H. Guo, A.V. Biradar, D.L. Peng, R. Zboril, R.S. Varma, *Chem. Soc. Rev.* 44 (2015) 7540–7590.
- [26] T. Mitsudome, Y. Mikami, M. Matoba, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Angew. Chem. Int. Ed.* 51 (2012) 136–139.
- [27] L. Zhang, D. Zhang, J. Zhang, S. Cai, C. Fang, L. Huang, H. Li, R. Gao, L. Shi, *Nanoscale* 5 (2013) 9821–9829.
- [28] S. Cai, H. Hu, H. Li, L. Shi, D. Zhang, *Nanoscale* 8 (2016) 3588–3598.
- [29] Z. Wu, M. Li, S.H. Overbury, *J. Catal.* 285 (2012) 61–73.
- [30] M. Li, Z. Wu, S.H. Overbury, *J. Catal.* 306 (2013) 164–176.
- [31] M. Honda, M. Tamura, Y. Nakagawa, K. Nakao, K. Suzuki, K. Tomishige, *J. Catal.* 318 (2014) 95–107.
- [32] M.D. Krcha, K.M. Dooley, M.J. Janik, *J. Catal.* 330 (2015) 167–176.
- [33] F. Gao, E.D. Walter, N.M. Washton, J. Szanyi, C.H.F. Peden, *Appl. Catal. B* 162 (2015) 501–514.
- [34] H. Huang, Y. Gu, J. Zhao, X. Wang, *J. Catal.* 326 (2015) 54–68.
- [35] P. Sudarsanam, B. Hillary, M.H. Amin, S.B.A. Hamid, S.K. Bhargava, *Appl. Catal. B* 185 (2016) 213–224.
- [36] H. Bao, Z. Zhang, Q. Hua, W. Huang, *Langmuir* 30 (2014) 6427–6436.
- [37] D. Zhang, A. Duan, Z. Zhao, C. Xu, *J. Catal.* 274 (2010) 273–286.
- [38] F. Liu, H. He, Z. Lian, W. Shan, L. Xie, K. Asakura, W. Yang, H. Deng, *J. Catal.* 307 (2013) 340–351.
- [39] S. Shwan, J. Jansson, L. Olsson, M. Skoglundh, *Appl. Catal. B* 166 (2015) 277–286.
- [40] W. Lai, Z. Chen, J. Zhu, L. Yang, J. Zheng, X. Yi, W. Fang, *Nanoscale* 8 (2016) 3823–3833.
- [41] S. Shwan, R. Nedyalkova, J. Jansson, J. Korsgren, L. Olsson, M. Skoglundh, *Ind. Eng. Chem. Res.* 51 (2012) 12762–12772.
- [42] X. Li, J. Li, Y. Peng, H. Chang, T. Zhang, S. Zhao, W. Si, J. Hao, *Appl. Catal. B* 184 (2016) 246–257.
- [43] H. Chang, X. Chen, J. Li, L. Ma, C. Wang, C. Liu, J.W. Schwank, J. Hao, *Environ. Sci. Technol.* 47 (2013) 5294–5301.
- [44] P.S. Miedema, F.M.F. de Groot, *J. Electron Spectrosc. Relat. Phenom.* 187 (2013) 32–48.
- [45] S.L. Yang, D.N. Wang, G.X. Liang, Y.M. Yiu, J.J. Wang, L.J. Liu, X.L. Sun, T.K. Sham, *Energy Environ. Sci.* 5 (2012) 7007–7016.
- [46] F. de Groot, *Coord. Chem. Rev.* 249 (2005) 31–63.
- [47] Y. Miyamoto, N. Katada, M. Niwa, *Microporous Mesoporous Mat.* 40 (2000) 271–281.
- [48] J. Liu, W. Song, C. Xu, J. Liu, Z. Zhao, Y. Wei, A. Duan, G. Jiang, *RSC Adv.* 5 (2015) 104923–104931.
- [49] S. Brandenberger, O. Kröcher, A. Wokaun, A. Tissler, R. Althoff, *J. Catal.* 268 (2009) 297–306.
- [50] W. Deng, Q. Dai, Y. Lao, B. Shi, X. Wang, *Appl. Catal. B* 181 (2016) 848–861.
- [51] G. Delahay, D. Valade, A. Guzman-Vargas, B. Coq, *Appl. Catal. B* 55 (2005) 149–155.
- [52] K. Skalska, J.S. Miller, S. Ledakowicz, *Sci. Total Environ.* 408 (2010) 3976–3989.
- [53] B. Jiang, B. Deng, Z. Zhang, Z. Wu, X. Tang, S. Yao, H. Lu, *J. Phys. Chem. C* 118 (2014) 14866–14875.
- [54] X. Shi, F. Liu, L. Xie, W. Shan, H. He, *Environ. Sci. Technol.* 47 (2013) 3293–3298.
- [55] W. Xu, H. He, Y. Yu, *J. Phys. Chem. C* 113 (2009) 4426–4432.
- [56] W. Yang, F. Liu, L. Xie, Z. Lian, H. He, *Ind. Eng. Chem. Res.* 55 (2016) 2677–2685.
- [57] J. Li, R. Zhu, Y. Cheng, C.K. Lambert, R.T. Yang, *Environ. Sci. Technol.* 44 (2010) 1799–1805.
- [58] L. Ma, J. Li, Y. Cheng, C.K. Lambert, L. Fu, *Environ. Sci. Technol.* 46 (2012) 1747–1754.
- [59] C. Sedlmair, K. Seshan, A. Jentys, J.A. Lercher, *J. Catal.* 214 (2003) 308–316.